

CH352 Assignment 2: Due Monday, 20 March 2017

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Q1 Ideal gas partition functions and thermodynamic quantities

The energy levels of a particle of mass m in a 1D box of length L_x are $E_{n_x} = n_x^2 h^2 / (8mL_x^2)$. Using the fact that the partition function for a particle moving in the x -direction is $q_x = \sum_{n_x} \exp[-\beta E_{n_x}]$, where $\beta = 1/(k_B T)$ and for a large box the energy levels are closely spaced so the sum can be replaced by an integral over a continuous version of the counter n , so that, $q_x = \sum_{n_x} e^{-\beta E_{n_x}} \sim \int_0^\infty dn e^{-\beta E_{n_x}}$, solve the following problems.

- (i) Compute the partition function for a particle moving in the x -direction.

$$\begin{aligned} q_x &= \int_0^\infty dn e^{-\beta E_{n_x}} \\ &= \int_0^\infty dn \exp\left(-\beta \frac{n^2 h^2}{8mL_x^2}\right) \end{aligned}$$

$$q_x = \sqrt{\frac{2\pi m L_x^2}{\beta h^2}}$$

- (ii) Use the fact that the energy levels of a particle moving in a three dimensional box are given by $E_{n_x, n_y, n_z} = E_{n_x} + E_{n_y} + E_{n_z}$ and your result from (i) to obtain an expression for the partition function, q , of a single particle moving in a three dimensional box. Give your final answer in terms of the volume of the box $V = L_x L_y L_z$.

$$\begin{aligned} q &= \int_0^\infty dn_x \int_0^\infty dn_y \int_0^\infty dn_z e^{-\beta E} \\ &= \int_0^\infty dn_x \int_0^\infty dn_y \int_0^\infty dn_z e^{-\beta(E_{n_x} + E_{n_y} + E_{n_z})} \\ &= \int_0^\infty dn_x e^{-\beta E_{n_x}} \int_0^\infty dn_y e^{-\beta E_{n_y}} \int_0^\infty dn_z e^{-\beta E_{n_z}} \end{aligned}$$

$$q = \frac{V}{h^3} \sqrt{\frac{8\pi^3 m^3}{\beta^3}}$$

- (iii) If particles moving in three dimensions do not interact with one another, as in the case of an ideal gas, the partition function, Q , of N non-interacting, identical particles can be shown to be the product of the partition functions of the individual particles: $Q = q^N/N!$ where the $N!$ factor accounts for the different possible ways of labeling the identical particles. Use your result from (ii) to obtain an expression for the N -particle partition function of an ideal gas.

$$Q = \frac{1}{N!} \left(\frac{V}{h^3} \sqrt{\frac{8\pi^3 m^3}{\beta^3}} \right)^N$$

- (iv) We can show that the internal energy of a system of N particles each moving in three dimensions can be obtained from the result

$$U = -\frac{1}{Q} \frac{\partial Q}{\partial \beta}. \quad (\text{Q1.1})$$

Using this result and your findings from (iii), obtain an expression for the internal energy of an ideal gas.

$$\frac{\partial Q}{\partial \beta} = \frac{\partial}{\partial \beta} \alpha \beta^{-3N/2}$$

where

$$\alpha = \frac{1}{N!} \left(\frac{V}{h^3} \sqrt{8\pi^3 m^3} \right)^N = \frac{Q}{\beta^{-3N/2}}$$

$$\frac{\partial Q}{\partial \beta} = -\frac{3N}{2} \alpha \beta^{(-3N/2)-1}$$

$$-\frac{1}{Q} \frac{\partial Q}{\partial \beta} = \frac{3N}{2\beta}$$

Q2 Entropy of an ideal gas

It can be shown that

$$\frac{p}{T} = \left(\frac{\partial S}{\partial V} \right)_{U,N}. \quad (\text{Q2.1})$$

Use this result to compute the entropy of an ideal gas to within an additive constant.

$$\begin{aligned}
\left(\frac{\partial S}{\partial V}\right)_{U,N} &= \frac{p}{T} \\
&= \frac{Nk_B}{V} \\
&\downarrow \\
S &= \int dV \frac{Nk_B}{V} \\
\boxed{S = Nk_B \ln V + C}
\end{aligned}$$

where C is some constant.

Q3 Temperature change over a waterfall

Our honeymooning scientist brings her thermometer with her in case her husband becomes ill. While out on a hike, she thinks to measure the temperature of water at the top and bottom of a local waterfall. The height of the waterfall is 500 m.

- (i) If all of the kinetic energy gained while falling is converted into heat and no heat is lost during the fall, what is the expected temperature change from the water at the top to the water at the bottom? The heat capacity of water is $4.184 \text{ J kg}^{-1} \text{ K}^{-1}$

$$\begin{aligned}
\Delta T &= \frac{mgh}{mC} \\
&= \frac{9.807 \text{ m s}^{-2} 500 \text{ m}}{4184 \text{ J kg}^{-1} \text{ K}^{-1}} \\
\boxed{\Delta T = 1.172 \text{ K}}
\end{aligned}$$

- (ii) If she measures the water at the top at a chilly 10.00°C , and the water at the bottom is 10.70°C , what percent of the kinetic energy was converted to thermal energy?

$$\frac{10.70 - 10.00}{1.172} \times 100\% = 59.7\%$$

- (iii) The scientist's new husband throws a 250 g snowball at 0°C at her while she's measuring the temperature of the water at the bottom of the waterfall; it misses her and lands in the water. What mass of water needs to fall over the waterfall to provide enough energy to melt the snowball? Use your efficiency calculated above. The enthalpy of fusion of water is 333.55 J g⁻¹.

$$E_{\text{melt}} = 250 \text{ g } 333.55 \text{ J g}^{-1} = 83.39 \text{ kJ}$$

$$m = \frac{E_{\text{melt}}}{C\Delta T}$$

$$= \frac{83.39 \text{ kJ}}{4.184 \text{ J g}^{-1} \text{ K}^{-1} 10.70 \text{ K}}$$

$$m = 1.862 \text{ kg}$$

Q4 Entropy changes are independent of process pathway.

Using your result for the entropy of an ideal gas from Q2:

- (i) Express $\Delta S_V = S_2(V_2) - S_1(V_1)$, the entropy change upon changing the volume from V_1 to V_2 at fixed particle number N .

$$\Delta S = Nk_B \ln V_2 + C - Nk_B \ln V_1 - C$$

$$\Delta S = Nk_B \ln \frac{V_2}{V_1}$$

- (ii) Express $\Delta S_N = S_2(N_2) - S_1(N_1)$, the entropy change upon changing the particle number from N_1 to N_2 , at fixed volume V .

$$\Delta S = N_2k_B \ln V + C - N_1k_B \ln V - C$$

$$\Delta S = (N_2 - N_1)k_B \ln V$$

- (iii) Write an expression for the entropy change, ΔS , for a two step process $(V_1, N_1) \rightarrow (V_2, N_1) \rightarrow (V_2, N_2)$ in which the volume changes first at fixed particle number then the particle number changes at fixed volume. Be sure to indicate the component entropy change for each step of the process.

$$\Delta S = N_2k_B \ln V_2 - N_1k_B \ln V_2 + N_1k_B \ln V_2 - N_1k_B \ln V_1$$

$$\Delta S = N_2k_B \ln V_2 - N_1k_B \ln V_1$$

- (iv) Show that the entropy change, ΔS , above is exactly the same as for the two step process in reverse order: changing the particle number first, then the volume.

$$\Delta S = N_2 k_B \ln V_2 - N_2 k_B \ln V_1 + N_2 k_B \ln V_1 - N_1 k_B \ln V_1$$

$$\boxed{\Delta S = N_2 k_B \ln V_2 - N_1 k_B \ln V_1}$$

Q5 Mechanical equilibrium equalizes density.

Consider a volume divided into M equal-size cells. The volume contains a movable piston that separates the left region, A , from the right region, B , so that at any instant the number of cells in the left region, M_A , and the number of cells in the right region, M_B , sum to give the total volume, $M_A + M_B = M$, which is fixed. Suppose the left region contains N_A particles and the right region contains N_B particles and that once a cell is occupied by a particle it cannot be occupied by any others (excluded volume!). Note that as the piston is moved to the right, expanding M_A , the shrinking size of region B can always be written in terms of M_A as $M_B = M - M_A$ using the constant total volume constraint.

- (i) Give general expressions for the multiplicities of states in regions A and B , that is W_A and W_B respectively, and write the total multiplicity $W = W_A W_B$ in terms of M_A alone using the above observation.

$$W_A = \frac{M_A!}{N_A!(M_A - N_A)!}$$

$$W_B = \frac{(M - M_A)!}{N_B!(M - M_A - N_B)!}$$

$$W = \frac{M_A!(M - M_A)!}{N_A!N_B!(M_A - N_A)!(M - M_A - N_B)!}$$

- (ii) To simplify the above results let's assume that the number of particles in any region, N , is always MUCH less than the number of cells in the volume, M , that is $N \ll M$. Your multiplicities in (i) should contain terms like $M!/(M - N)!$. Show that these terms can be simplified under these conditions and approximated as

$$\lim_{N \ll M} \frac{M!}{(M - N)!} \sim M^N. \quad (\text{Q5.1})$$

$$\begin{aligned} \lim_{N \ll M} \frac{M!}{(M - N)!} &\sim \left(\frac{M}{e}\right)^M \left(\frac{e}{M - N}\right)^{M - N} \\ &\sim \frac{M^M}{e^N} \frac{1}{M^{M - N}} \end{aligned}$$

$$\boxed{\lim_{N \ll M} \frac{M!}{(M - N)!} \sim M^N}$$

- (iii) Use the result from (ii) to simplify your expression from (i) and obtain an approximate expression for the entropy $S = k_B \ln W$ written in terms of M_A . Find the value of $M_A = M_A^*$ that maximizes S , and show that at equilibrium the piston will move to equalize the density of particles on each side.

$$W \sim \frac{M_A^{N_A} (M - M_A)^{N_B}}{N_A! N_B!}$$

$$S = k_B (N_A \ln M_A + N_B \ln(M - M_A) - \ln N_A! - \ln N_B!)$$

$$\frac{1}{k_B} \frac{\partial S}{\partial M_A} = 0 = \frac{N_A}{M_A^*} - \frac{N_B}{M - M_A^*}$$

$$M - M_A^* = \frac{N_B}{N_A} M_A^*$$

$$M_A^* = M \frac{N_A}{N_A + N_B}$$

$$\frac{N_A}{M_A} = \frac{N_A + N_B}{M}$$

$$\frac{N_B}{M - M_A} = \frac{N_B}{M - M \frac{N_A}{N_A + N_B}}$$

$$= \frac{(N_A + N_B) N_B}{M N_B}$$

$$\therefore$$

$$\frac{N_A}{M_A} = \frac{N_B}{M - M_A}$$